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<p>(21) International Application Number: <b>PCT/US94/05372</b></p> <p>(22) International Filing Date: <b>12 May 1994 (12.05.94)</b></p> <p>(30) Priority Data:</p> <table border="0"><tr><td><b>08/064,563</b></td><td><b>20 May 1993 (20.05.93)</b></td><td><b>US</b></td></tr><tr><td><b>08/133,691</b></td><td><b>7 October 1993 (07.10.93)</b></td><td><b>US</b></td></tr><tr><td><b>08/151,316</b></td><td><b>12 November 1993 (12.11.93)</b></td><td><b>US</b></td></tr><tr><td><b>08/196,322</b></td><td><b>15 February 1994 (15.02.94)</b></td><td><b>US</b></td></tr></table> <p>(71) Applicant: <b>THE PROCTER &amp; GAMBLE COMPANY</b> [US/US]; One Procter &amp; Gamble Plaza, Cincinnati, OH 45202 (US).</p> <p>(72) Inventors: <b>WILLEY, Alan, David</b>; 1071 Celestial Street, Cincinnati, OH 45202 (US). <b>BURNS, Michael, Eugene</b>; 9248 Sunderland Way, West Chester, OH 45069 (US). <b>HARTSHORN, Richard, Timothy</b>; 8 Hersham Close, Kingston Park, Newcastle upon Tyne NE3 2TN (GB). <b>GHOSH, Chanchal, Kumar</b>; 7005 Pinemill Drive, West Chester, OH 45069 (US).</p> <p>(74) Agents: <b>REED, T., David et al.</b>; The Procter &amp; Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45202 (US).</p>		<b>08/064,563</b>	<b>20 May 1993 (20.05.93)</b>	<b>US</b>	<b>08/133,691</b>	<b>7 October 1993 (07.10.93)</b>	<b>US</b>	<b>08/151,316</b>	<b>12 November 1993 (12.11.93)</b>	<b>US</b>	<b>08/196,322</b>	<b>15 February 1994 (15.02.94)</b>	<b>US</b>	<p>(81) Designated States: AU, BB, BG, BR, BY, CA, CN, CZ, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LV, MD, MG, MN, MW, NO, NZ, PL, RO, RU, SD, SI, SK, TJ, TT, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
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<p>(54) Title: <b>BLEACHING COMPOUNDS COMPRISING PEROXYACID ACTIVATORS USED WITH ENZYMES</b></p> <p>(57) Abstract</p> <p>The present invention relates to laundry detergent compositions comprising conventional detergent ingredients, bleaching systems with one or more bleach activators, and one or more types of detergent enzymes. Preferred bleaching activators are amido-derived bleach activators and/or N-acyl caprolactam bleach activators. The invention also relates to methods of using the detergent compositions.</p>														

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BLEACHING COMPOUNDS COMPRISING  
PEROXYACID ACTIVATORS USED WITH ENZYMES

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FIELD OF THE INVENTION

10       The present invention relates to laundry detergents and methods which employ one or more types of detergent enzymes and a bleaching system with one or more bleach activators.

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BACKGROUND OF THE INVENTION

20       Various types of detergent enzymes have long been conventionally used in laundry detergents to assist in the removal of certain stains from fabrics. These stains are typically associated with lipid and protein soils. The enzymes, however, have proven less effective against other types of soils and stains.

It has also long been known that peroxygen bleaches are effective for stain  
25 and/or soil removal from fabrics, but that such bleaches are temperature dependent. At a laundry liquor temperature of 60°C, peroxygen bleaches are only partially effective. As the laundry liquor temperature is lowered below 60°C, peroxygen bleaches become relatively ineffective. As a consequence, there has been a substantial amount of industrial research to develop bleaching systems which contain  
30 an activator that renders peroxygen bleaches effective at laundry liquor temperatures below 60°C.

Numerous substances have been disclosed in the art as effective bleach  
activators. One widely-used activator is tetraacetyl ethylene diamine (TAED).  
TAED provides effective hydrophilic cleaning especially on beverage stains, but has  
35 limited performance on dingy, yellow stains such as those resulting from body oils. Fortunately, another type of activator, such as nonanoyloxybenzenesulfonate (NOBS) and other activators which generally comprise long chain alkyl moieties, is

hydrophobic in nature and provides excellent performance on dingy stains.

It would seem that a combination of enzymes with either hydrophilic or hydrophobic bleach activators, or both, would provide an effective "all-around" detergent composition which would perform well on most types of soils and stains. However, a hindrance to the development of such all-around cleaning compositions has been the discovery that many of the hydrophobic bleach activators developed thus far can promote damage to natural rubber parts used in certain washing machines. Because of the negative effects on washing machine parts, the selection of such detergent-added bleaching systems has been limited. This is especially true for European detergent/bleaches, since many washing machines manufactured in Europe are equipped with key parts, such as sump hoses and motor gaskets, made of natural rubber.

Another problem in developing an all-around cleaning composition has been finding a cleaning agent that is effective under heavy soil load conditions. The removal of heavy soil levels, especially nucleophilic and body soils, has proven especially difficult for conventional bleaching systems. Under such circumstances, conventional activators such as NOBS appear to interact with, and be destroyed by, heavy soil loads before they can optimally provide their intended bleaching function. Still another problem has been the stability of enzymes, especially lipases and proteases, in the presence of bleaches.

A need, therefore, exists for a stable detergent composition which provides effective cleaning performance over a wide variety of soils and stains. Moreover, the detergent composition should provide effective cleaning performance without substantially damaging natural rubber machine parts. In addition, the compositions should provide both bleaching performance and enzyme cleaning performance.

Without intending to be limited by theory, it is believed that typical hydrophobic bleach activators undergo a perhydrolysis reaction to form a peroxyacid bleaching agent. However, a typical by-product of the perhydrolysis reaction between conventional bleach activators and hydrogen peroxide is a diacylperoxide (DAP) species. Unfortunately, DAP species derived from hydrophobic activators tend to be insoluble, poorly dispersible, oily materials which form a residue which can deposit on the natural rubber machine parts that are exposed to the laundry liquor. The oily DAP residue can form a film on the natural rubber machine parts and promote free radical and peroxide damage to the rubber, which eventually leads to failure of the parts.

By the present invention, it has now been discovered that the class of hydrophobic bleach activators derived from amido acids forms hydrophobic amido

peracids upon perhydrolysis without the production of harmful, oily DAP's. Again, while not intending to be limited by theory, it is believed that the DAP's produced by the perhydrolysis reaction of the amido acid-derived bleach activators used herein are insoluble crystalline solids. The solids do not form a coating film; therefore, the natural rubber parts are not exposed to the DAP's for extended periods of time and remain substantially undamaged.

In addition to the amido acid-derived bleach activators, it has also now been discovered that the class of bleach activators derived from N-acyl caprolactams provide both hydrophilic and hydrophobic bleaching action without the production of harmful DAP by-products.

Additionally, it has also now been discovered that the class of benzoxazin-type bleach activators provide effective hydrophobic bleaching action without the production of harmful DAP by-products.

Surprisingly, it has also been discovered that certain enzymes, particularly lipase enzymes, are compatible with said classes of bleach activators.

Accordingly, the present invention solves the long-standing need for detergent compositions which provide efficient and effective performance over a wide range of cleaning needs by combining the cleaning actions of enzymes with the hydrophobic cleaning action of amido derived bleach activators or with the hydrophobic and hydrophilic cleaning action of N-acyl caprolactam bleach activators. The invention also provides efficient and effective detergent compositions for use in washing machines which have parts made of natural rubber, such that the natural rubber is substantially undamaged by the bleaching system. These and other benefits are secured by the invention, as will be seen hereinafter.

#### BACKGROUND ART

U.S. Patent 4,634,551, Burns et al, issued January 6, 1987, discloses amido peroxyacid bleaching compounds and their precursors which are employed in the present invention. See also, U.S. Patent 4,852,989, Burns et al, issued August 1, 1989. U.S. Patent 5,069,809, Lagerwaard et al, issued Dec. 3, 1991 discloses the combination of NOBS bleach activators with LIPOLASE, lipase enzymes. See E.P. Patent 341,947, Lagerwaard, et al, published November 15, 1989 for a discussion of the compatibility problems of lipase enzymes with certain bleaching systems. U.S. Patent 4,545,784, Sanderson, issued October 8, 1985, discloses the absorption of activators onto sodium perborate monohydrate.

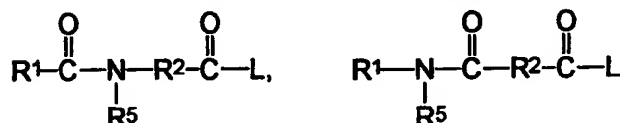
#### SUMMARY OF THE INVENTION

The invention herein provides cleaning compositions and methods which are safe for use in contact with natural rubber, and which provide not only bleach

performance, but also good detergent enzyme stability and performance.

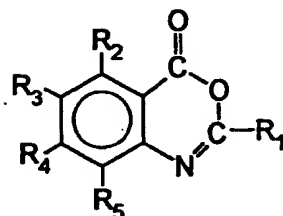
The present invention encompasses detergent compositions comprising an effective amount of one or more types of enzymes and a bleaching system comprising at least about 0.1%, by weight, of a peroxygen bleaching compound and at least  
5 about 0.1%, by weight, of one or more bleach activators, wherein said bleach activators are members selected from the group consisting of:

a) a bleach activator of the general formula:



or mixtures thereof, wherein  $\text{R}^1$  is an alkyl, aryl, or alkaryl group  
10 containing from about 1 to about 14 carbon atoms,  $\text{R}^2$  is an alkylene, arylene or alkarylene group containing from about 1 to about 14 carbon atoms,  $\text{R}^5$  is H or an alkyl, aryl, or alkaryl group containing from about 1 to about 10 carbon atoms, and L is a leaving group;

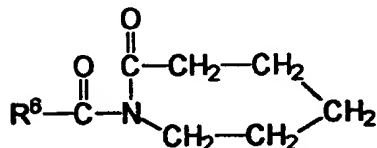
b) benzoxazin-type bleach activators of the general formula:



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wherein  $\text{R}_1$  is H, alkyl, alkaryl, aryl, arylalkyl, and wherein  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$ , and  $\text{R}_5$  may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxy, amino, alkylamino,  $\text{COOR}_6$  (wherein  $\text{R}_6$  is H or an alkyl group) and carbonyl functions;

20 c) N-acyl caprolactam bleach activators of the formula:

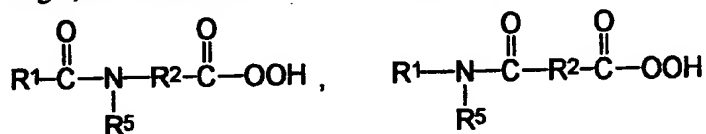


wherein  $\text{R}^6$  is H or an alkyl, aryl, alkoxyaryl or alkaryl group containing from 1 to 12 carbons; and

d) mixtures of a), b) and c).

25 Preferably, the molar ratio of hydrogen peroxide yielded by the peroxygen bleaching compound to bleach activator is greater than about 1.0. Most preferably, the molar ratio of hydrogen peroxide to bleach activator is at least about 1.5.

The present invention also encompasses detergent compositions comprising an effective amount of one or more types of enzymes and a bleaching system comprising at least about 0.1%, preferably from about 0.1% to about 50%, by weight, of a substantially insoluble organic peroxyacid having the general formula:



wherein  $\text{R}^1$ ,  $\text{R}^2$ , and  $\text{R}^5$  are as defined for the type a) bleach activator above.

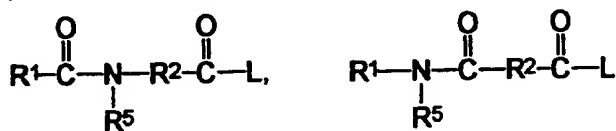
Preferred bleach activators of type a) are those wherein  $\text{R}^1$  is an alkyl group containing from about 6 to about 12 carbon atoms,  $\text{R}^2$  contains from about 1 to about 8 carbon atoms, and  $\text{R}^5$  is H or methyl. Particularly preferred bleach activators are those of the above general formulas wherein  $\text{R}^1$  is an alkyl group containing from about 7 to about 10 carbon atoms and  $\text{R}^2$  contains from about 4 to about 5 carbon atoms.

Preferred bleach activators of type b) are those wherein  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$ , and  $\text{R}_5$  are H and  $\text{R}_1$  is a phenyl group.

The preferred acyl moieties of said N-acyl caprolactam bleach activators of type c) have the formula  $\text{R}^6-\text{CO}-$  wherein  $\text{R}^6$  is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbons, preferably from 6 to 12 carbon atoms. In highly preferred embodiments,  $\text{R}^6$  is a member selected from the group consisting of phenyl, heptyl, octyl, nonyl, 2,4,4-trimethylpentyl, decenyl and mixtures thereof.

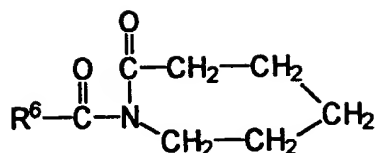
Other highly preferred detergent compositions are those comprising bleach activators selected from the group consisting of:

a) a bleach activator of the formula:



or mixtures thereof, wherein  $\text{R}^1$  is an alkyl, aryl, or alkaryl group containing from about 1 to about 14 carbon atoms,  $\text{R}^2$  is an alkylene, arylene or alkarylene group containing from about 1 to about 14 carbon atoms,  $\text{R}^5$  is H or an alkyl, aryl, or alkaryl group containing from about 1 to about 10 carbon atoms, and L is a leaving group;

b) a N-acyl caprolactam bleach activator of the formula:



wherein R<sup>6</sup> is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from about 1 to about 12 carbons; and

c) mixtures of a) and b);

5 and an enzyme selected from the group consisting of SAVINASE, Protease C, and mixtures thereof. Highly preferred activators include benzoyl caprolactam, nona-nonyl caprolactam, (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxy-benzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof.

10 The peroxygen bleaching compound can be any peroxide source, and is preferably a member selected from the group consisting of sodium perborate monohydrate, sodium perborate tetrahydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium percarbonate, sodium peroxide and mixtures thereof. Preferred peroxygen bleaching compounds are selected from the group consisting of

15 sodium perborate monohydrate, sodium percarbonate, sodium perborate tetrahydrate and mixtures thereof. A highly preferred peroxygen bleaching compound is sodium percarbonate.

The amido-derived and caprolactam bleach activators herein can also be used in combination with rubber-safe, enzyme-safe, hydrophilic activators such as TAED, typically at weight ratios of amido-derived or caprolactam activators:TAED in the range of 1:5 to 5:1, preferably about 1:1.

The compositions and uses herein are effective with all manner of detergent enzymes, e.g., members selected from the group consisting of proteases, amylases, lipases, cellulases, peroxidases and mixtures thereof. Highly preferred are lipase enzymes derived from the fungus Humicola lanuginosa, optionally as expressed in Aspergillus oryzae as host using art-disclosed genetic engineering techniques. Also highly preferred are modified protease bacterial serine protease enzymes obtained from Bacillus subtilis, Bacillus lentus or Bacillus licheniformis. Said enzymes comprise at least about 0.001%, preferably from about 0.001% to about 5%, of the detergent compositions.

The invention also encompasses a method for cleaning fabrics comprising contacting, preferably with agitation, said fabrics with an aqueous liquor containing said detergent composition. The method can be carried out at temperatures below about 60°C but, of course, is quite effective and is still safe to rubber parts at laundry



temperatures up to the boil. The aqueous laundry liquor comprises at least about 300 ppm of conventional detergent ingredients, as well as at least about 25 ppm of bleach activator and at least about 25 ppm of bleaching compound. Preferably, said aqueous liquor comprises from about 900 ppm to about 20,000 ppm of the conventional detergent ingredients, from about 100 ppm to about 25,000 ppm of bleaching compound and from about 100 ppm to about 2,500 ppm of said bleach activator.

The conventional detergent ingredients employed in said method comprise from about 1% to about 99.8%, preferably from about 5% to about 80%, of a deterative surfactant. Optionally, deterative compositions can also comprise from about 5% to about 80% of a detergent builder. Other optional deterative ingredients are also encompassed by the fully-formulated detergent/bleach compositions provided by this invention.

All percentages, ratios and proportions are by weight, unless otherwise specified. All documents cited are incorporated herein by reference.

#### DETAILED DESCRIPTION OF THE INVENTION

The detergent compositions employed in the present invention provide effective and efficient surface cleaning of fabrics which thereby removes stains and/or soils from the fabrics. The bleaching systems in combination with one or more types of enzymes are particularly efficient at removing most types of soils from the fabrics, including protein and lipid soils, dingy soils, and heavy soil loads, especially from nucleophilic and body soils.

The superior bleaching/cleaning action of the present compositions is achieved with safety to natural rubber machine parts and other natural rubber articles, including fabrics containing natural rubber and natural rubber elastic materials. The bleaching mechanism and, in particular, the surface bleaching mechanism are not completely understood. However, it is generally believed that the bleach activator undergoes nucleophilic attack by a perhydroxide anion, which is generated from the hydrogen peroxide evolved by the peroxygen bleach, to form a peroxycarboxylic acid. This reaction is commonly referred to as perhydrolysis.

The bleaching systems and activators herein afford additional advantages in that, unexpectedly, they are safer to fabrics and cause less color damage than other activators when used in the manner provided by this invention.

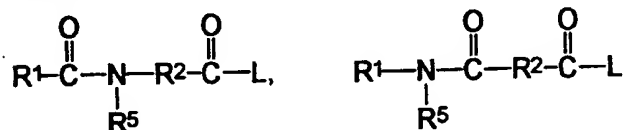
It is also believed that the bleach activators within the invention can render peroxygen bleaches more efficient even at laundry liquor temperatures wherein bleach activators are not necessary to activate the bleach, i.e., above about 60°C. Therefore, with bleach systems of the invention, less peroxygen bleach is required t

get the same level of surface bleaching performance as is obtained with the peroxygen bleach alone.

The bleaching systems, wherein the bleach activator is used, also have as an essential component a peroxygen bleach capable of releasing hydrogen peroxide in aqueous solution.

#### The Bleach Activator

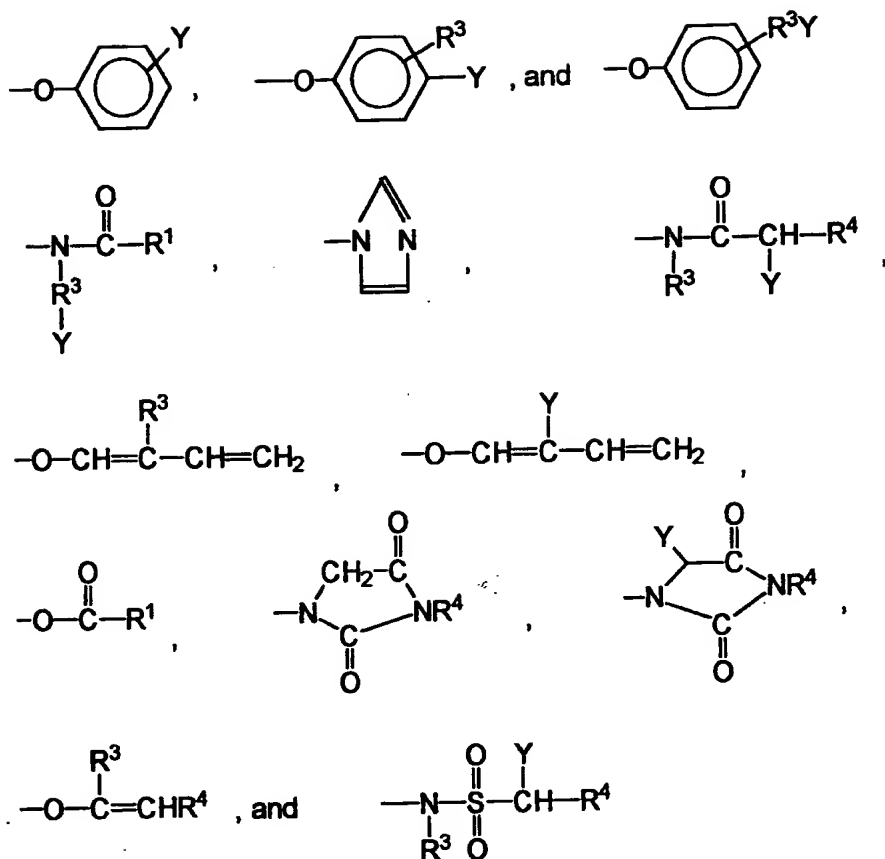
Amido Derived Bleach Activators - The bleach activators of type a) employed in the present invention are amide substituted compounds of the general formulas:



or mixtures thereof, wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^5$  are as defined above and L can be essentially any suitable leaving group. A leaving group is any group that is displaced from the bleaching activator as a consequence of the nucleophilic attack on the bleach activator by the perhydroxide anion. This, the perhydrolysis reaction, results in the formation of the peroxycarboxylic acid. Generally, for a group to be a suitable leaving group it must exert an electron attracting effect. It should also form a stable entity so that the rate of the back reaction is negligible. This facilitates the nucleophilic attack by the perhydroxide anion.

The L group must be sufficiently reactive for the reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition. These characteristics are generally paralleled by the pKa of the conjugate acid of the leaving group, although exceptions to this convention are known. Ordinarily, leaving groups that exhibit such behavior are those in which their conjugate acid has a pKa in the range of from about 4 to about 13, preferably from about 6 to about 11 and most preferably from about 8 to about 11.

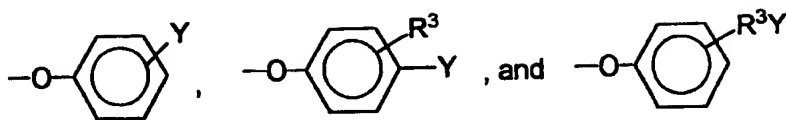
Preferred bleach activators are those of the above general formula wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^5$  are as defined for the peroxyacid and L is selected from the group consisting of:



- 5 and mixtures thereof, wherein R<sup>1</sup> is an alkyl, aryl, or alkaryl group containing from about 1 to about 14 carbon atoms, R<sup>3</sup> is an alkyl chain containing from 1 to about 8 carbon atoms, R<sup>4</sup> is H or R<sup>3</sup>, and Y is H or a solubilizing group.

The preferred solubilizing groups are -SO<sub>3</sub><sup>-</sup>M<sup>+</sup>, -CO<sub>2</sub><sup>-</sup>M<sup>+</sup>, -SO<sub>4</sub><sup>-</sup>M<sup>+</sup>, -N<sup>+</sup>(R<sup>3</sup>)<sub>4</sub>X<sup>-</sup> and O<-N(R<sup>3</sup>)<sub>3</sub> and most preferably -SO<sub>3</sub><sup>-</sup>M<sup>+</sup> and -CO<sub>2</sub><sup>-</sup>M<sup>+</sup> wherein  
 10 R<sup>3</sup> is an alkyl chain containing from about 1 to about 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and  
 15 X is a halide, hydroxide, methylsulfate or acetate anion. It should be noted that bleach activators with a leaving group that does not contain a solubilizing groups should be well dispersed in the bleaching solution in order to assist in their dissolution.

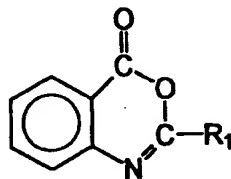
Preferred bleach activators are those of the above general formula wherein L is selected from the group consisting of:



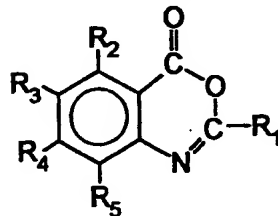
wherein  $R^3$  is as defined above and Y is  $-\text{SO}_3^- \text{M}^+$  or  $-\text{CO}_2^- \text{M}^+$  wherein M is as defined above.

Another important class of bleach activators, including those of type b) and type c), provide organic peracids as described herein by ring-opening as a consequence of the nucleophilic attack on the carbonyl carbon of the cyclic ring by the perhydroxide anion. For instance, this ring-opening reaction in type c) activators involves attack at the caprolactam ring carbonyl by hydrogen peroxide or its anion. Since attack of an acyl caprolactam by hydrogen peroxide or its anion occurs preferably at the exocyclic carbonyl, obtaining a significant fraction of ring-opening may require a catalyst. Another example of ring-opening bleach activators can be found in type b) activators, such as those disclosed in U.S. Patent 4,966,723, Hodge et al, issued Oct. 30, 1990.

Such activator compounds disclosed by Hodge include the activators of the benzoxazin-type, having the formula:



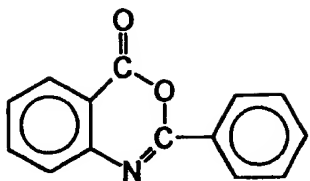
including the substituted benzoxazins of the type



wherein  $R_1$  is H, alkyl, alkaryl, aryl, arylalkyl, and wherein  $R_2$ ,  $R_3$ ,  $R_4$ , and  $R_5$  may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxy, amino, alkyl amino,  $\text{COOR}_6$  (wherein  $R_6$  is H or an alkyl group) and carbonyl functions.

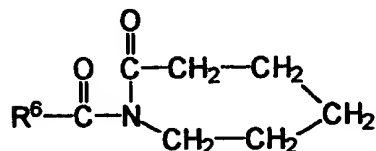
A preferred activator of the benzoxazin-type is:

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When the activators are used, optimum surface bleaching performance is obtained with washing solutions wherein the pH of such solution is between about 8.5 and 10.5 and preferably between 9.5 and 10.5 in order to facilitate the perhydrolysis reaction. Such pH can be obtained with substances commonly known as buffering agents, which are optional components of the bleaching systems herein.

The N-Acyl Caprolactam Bleach Activators - The N-acyl caprolactam bleach activators of type c) employed in the present invention have the formula:



wherein  $R^6$  is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbons. Caprolactam activators wherein the  $R^6$  moiety contains at least about 6, preferably from 6 to about 12, carbon atoms provide hydrophobic bleaching which affords nucleophilic and body soil clean-up, as noted above. Caprolactam activators wherein  $R^6$  comprises from 1 to about 6 carbon atoms provide hydrophilic bleaching species which are particularly efficient for bleaching beverage stains. Mixtures of hydrophobic and hydrophilic caprolactams, typically at weight ratios of 1:5 to 5:1, preferably 1:1, can be used herein for mixed stain removal benefits.

Highly preferred N-acyl caprolactams are selected from the group consisting of benzoyl caprolactam, octanoyl caprolactam, nonanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, and mixtures thereof.

Methods for making N-acyl caprolactams are well known in the art. Examples I and II, included below, illustrate preferred laboratory syntheses.

Contrary to the teachings of U.S. Pat. 4,545,784, cited above, the bleach activator is preferably not absorbed onto the peroxygen bleaching compound. To do so in the presence of other organic detergent ingredients could cause safety problems.

The bleach activators of type a), b) or c) will comprise at least about 0.1%, preferably from about 0.1% to about 50%, more preferably from about 1% to about 30%, most preferably from about 3% to about 25%, by weight of bleaching system or detergent composition.

When the activators are used, optimum surface bleaching performance is obtained with washing solutions wherein the pH of such solution is between about 8.5 and 10.5 and preferably between 9.5 and 10.5 in order to facilitate the perhydrolysis reaction. Such pH can be obtained with substances commonly known as buffering agents, which are optional components of the bleaching systems herein.

#### The Peroxygen Bleaching Compound

The peroxygen bleaching systems useful herein are those capable of yielding hydrogen peroxide in an aqueous liquor. These compounds are well known in the art and include hydrogen peroxide and the alkali metal peroxides, organic peroxide bleaching compounds such as urea peroxide, and inorganic persalt bleaching compounds, such as the alkali metal perborates, percarbonates, perphosphates, and the like. Mixtures of two or more such bleaching compounds can also be used, if desired.

Preferred peroxygen bleaching compounds include sodium perborate, commercially available in the form of mono-, tri-, and tetra-hydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium percarbonate, and sodium peroxide. Particularly preferred are sodium perborate tetrahydrate, sodium perborate monohydrate and sodium percarbonate. Percarbonate is especially preferred because it is very stable during storage and yet still dissolves very quickly in the bleaching liquor. It is believed that such rapid dissolution results in the formation of higher levels of percarboxylic acid and, thus, enhanced surface bleaching performance.

Highly preferred percarbonate can be in uncoated or coated form. The average particle size of uncoated percarbonate ranges from about 400 to about 1200 microns, most preferably from about 400 to about 600 microns. If coated percarbonate is used, the preferred coating materials include mixtures of carbonate and sulphate, silicate, borosilicate, or fatty carboxylic acids.

The peroxygen bleaching compound will comprise at least about 0.1%, preferably from about 1% to about 75%, more preferably from about 3% to about 40%, most preferably from about 3% to about 25%, by weight of bleaching system or detergent composition.

The weight ratio of bleach activator to peroxygen bleaching compound in the bleaching system typically ranges from about 2:1 to 1:5. Preferred ratios range from about 1:1 to about 1:3.

The bleach activator/bleaching compound systems herein are useful per se as bleaches. However, such bleaching systems are especially useful in compositions which can comprise various deterative adjuncts such as surfactants, builders and the like.

### The Deterasive Enzymes

The deterasive enzymes of the present invention are included for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of fugitive dye transfer. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability, stability versus active detergents, builders and so on. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to about 50 mg by weight, more typically about 0.01 mg to about 10 mg, of active enzyme per gram of detergent composition. Stated otherwise, an effective amount of the enzymes employed in the present invention will comprise at least about 0.001%, preferably from about 0.001% to about 5%, more preferably from about 0.001% to about 1%, most preferably from about 0.01% to about 1%, by weight of detergent composition.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B.subtilis*, *B.lentus* and *B.licheniforms*. Another suitable protease is a modified bacterial serine protease enzyme obtained from *Bacillus subtilis* or *Bacillus licheniformis*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in British Patent Specification No. 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see European Patent Application 130,756, published January 9, 1985) and Protease B (see European Patent Application Serial No. 87303761.8, filed April 28, 1987, and European Patent Application 130,756, Bott et al, published January 9, 1985). Most preferred is what is called herein "Protease C", which is a variant of an alkaline serine protease from *Bacillus*, particularly *Bacillus lentus*, in which arginine replaced lysine at position 27, tyrosine replaced valine at position 104, serine replaced asparagine at position 123, and alanine replaced threonine at position 274. Protease C is described in EP 90915958:4, U.S. Patent No. 5,185,250 and U.S. Patent No. 5,204,015, which are

incorporated herein by reference. Genetically modified variants, particularly of Protease C, are also included herein.

Amylases include, for example,  $\alpha$ -amylases described in British Patent Specification No. 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, Barbesgoard et al, issued March 6, 1984, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in British Patent 1,372,034. See also lipases in Japanese Patent Application 53-20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano," hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynt Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme, derived from the fungus *Humicola lanuginosa* and expressed in *Aspergillus oryzae* as host and commercially available from Novo (see also E.P. Patent 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent granules is also disclosed in U.S. Patent 3,553,139, issued



January 5, 1971 to McCarty et al. Enzymes are further disclosed in U.S. Patent 4,101,457, Place et al, issued July 18, 1978, and in U.S. Patent 4,507,219, Hughes, issued March 26, 1985, both. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868, Hora et al, issued April 14, 1981. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilization techniques are disclosed and exemplified in U.S. Patent 4,261,868, issued April 14, 1981 to Horn, et al, U.S. Patent 3,600,319, issued August 17, 1971 to Gedge, et al, and European Patent Application Publication No. 0199405, Application No. 86200586.5, published October 29, 1986, Venegas. Enzyme stabilization systems are also described, for example, in U.S. Patents 4,261,868, 3,600,319, and 3,519,570.

Enzyme Stabilizers - The enzymes employed herein are stabilized by the presence of water-soluble sources of calcium ions in the finished compositions which provide calcium ions to the enzymes. Additional stability can be provided by the presence of various other art-disclosed stabilizers, especially borate species: see Severson, U.S. 4,537,706, cited above. Typical detergents, especially liquids, will comprise from about 1 to about 30, preferably from about 2 to about 20, more preferably from about 5 to about 15, and most preferably from about 8 to about 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium ions. The level of calcium ion should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium salt can be used as the source of calcium ion, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium hydroxide, calcium formate, and calcium acetate. A small amount of calcium ion, generally from about 0.05 to about 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

The compositions herein may also optionally, but preferably, contain various additional stabilizers including silicate coatings and, especially borate-type stabilizers. Typically, such stabilizers will be used at levels in the compositions from about 0.25% to about 10%, preferably from about 0.5% to about 5%, more preferably from about 0.75% to about 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and

other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

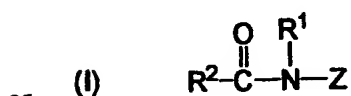
#### Deterstive Surfactant

5 The amount of deterstive surfactant included in the fully-formulated detergent compositions afforded by the present invention can vary from about 1% to about 99.8% depending upon the particular surfactants used and the effects desired. Preferably, the deterstive surfactants comprise from about 5% to about 80% by  
10 weight of the detergent ingredients.

The deterstive surfactant can be nonionic, anionic, ampholytic, zwitterionic, or cationic. Mixtures of these surfactants can also be used. Preferred detergent compositions comprise anionic deterstive surfactants or mixtures of anionic surfactants with other surfactants, especially nonionic surfactants.

15 Nonlimiting examples of surfactants useful herein include the conventional C<sub>11</sub>-C<sub>18</sub> alkyl benzene sulfonates and primary, secondary, and random alkyl sulfates, the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates, the C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, C<sub>12</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters, C<sub>12</sub>-C<sub>18</sub> alkyl and alkyl phenol alkoxyates (especially ethoxylates and mixed  
20 ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, and the like. Other conventional useful surfactants are listed in standard texts.

One particular class of adjunct nonionic surfactants especially useful herein comprises the polyhydroxy fatty acid amides of the formula:



wherein: R<sup>1</sup> is H, C<sub>1</sub>-C<sub>8</sub> hydrocarbyl, 2-hydroxyethyl, 2-hydroxypropyl, or a mixture thereof, preferably C<sub>1</sub>-C<sub>4</sub> alkyl, more preferably C<sub>1</sub> or C<sub>2</sub> alkyl, most preferably C<sub>1</sub> alkyl (i.e., methyl); and R<sup>2</sup> is a C<sub>5</sub>-C<sub>32</sub> hydrocarbyl moiety, preferably straight chain C<sub>7</sub>-C<sub>19</sub> alkyl or alkenyl, more preferably straight chain C<sub>9</sub>-C<sub>17</sub> alkyl  
30 or alkenyl, most preferably straight chain C<sub>11</sub>-C<sub>19</sub> alkyl or alkenyl, or mixture thereof; and Z is a polyhydroxyhydrocarbyl moiety having a linear hydrocarbyl chain with at least 2 (in the case of glyceraldehyde) or at least 3 hydroxyls (in the case of other reducing sugars) directly connected to the chain, or an alkoxyated derivative (preferably ethoxyated or propoxyated) thereof. Z preferably will be derived from a  
35 reducing sugar in a reductive amination reaction; more preferably Z is a glyceryl

moiety. Suitable reducing sugars include glucose, fructose, maltose, lactose, galactose, mannose, and xylose, as well as glyceraldehyde. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilized as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of  $-\text{CH}_2-(\text{CHOH})_n-\text{CH}_2\text{OH}$ ,  $-\text{CH}(\text{CH}_2\text{OH})-(\text{CHOH})_{n-1}-\text{CH}_2\text{OH}$ ,  $-\text{CH}_2-(\text{CHOH})_2(\text{CHOR}')(\text{CHOH})-\text{CH}_2\text{OH}$ , where n is an integer from 1 to 5, inclusive, and R' is H or a cyclic mono- or poly- saccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly  $-\text{CH}_2-(\text{CHOH})_4\text{CH}_2\text{OH}$ .

In Formula (I),  $\text{R}^1$  can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-isobutyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. For highest sudsing,  $\text{R}^1$  is preferably methyl or hydroxyalkyl. If lower sudsing is desired,  $\text{R}^1$  is preferably  $\text{C}_2$ - $\text{C}_8$  alkyl, especially n-propyl, iso-propyl, n-butyl, iso-butyl, pentyl, hexyl and 2-ethyl hexyl.

$\text{R}^2-\text{CO}-\text{N}<$  can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide, etc.

#### Detersive Builders

Optional detergent ingredients employed in the present invention contain inorganic and/or organic detersive builders to assist in mineral hardness control. If used, these builders comprise from about 5% to about 80% by weight of the detergent compositions.

Inorganic detersive builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the triphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, nonphosphate builders are required in some locales.

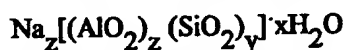
Examples of silicate builders are the alkali metal silicates, particularly those having a  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio in the range 1.6:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839, issued May 12, 1987 to H. P. Rieck, available from Hoechst under the trademark "SKS"; SKS-6 is an especially preferred layered silicate builder.

Carbonate builders, especially a finely ground calcium carbonate with surface area greater than  $10 \text{ m}^2/\text{g}$ , are preferred builders that can be used in granular compositions. The density of such alkali metal carbonate built detergents can be in

the range of 450-850 g/l with the moisture content preferably below 4%.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

- 5 Aluminosilicate builders are especially useful in the present invention. Preferred aluminosilicates are zeolite builders which have the formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to about 0.5, and x is an integer from about 15 to about 264.

- 10 Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. Methods for producing aluminosilicate ion exchange materials are disclosed in U.S. Patent 3,985,669, Krummel, et al, issued October 12, 1976, and U.S. Patent 4,605,509, Corkill, et al,  
15 issued Aug. 12, 1986. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B) (including those disclosed in EPO 384,070), and Zeolite X. Preferably, the aluminosilicate has a particle size of about 0.1-10 microns in diameter.

- Organic deterative builders suitable for the purposes of the present invention  
20 include, but are not restricted to, a wide variety of polycarboxylate compounds, such as ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. Patent 3,128,287, issued April 7, 1964, and Lamberti et al, U.S. Patent 3,635,830, issued January 18, 1972. See also "TMS/TDS" builders of U.S. Patent 4,663,071, issued to Bush et al, on May 5, 1987. Suitable ether polycarboxylates also include cyclic  
25 compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

- Other useful deterative builders include the ether hydroxy-polycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyl-oxysuccinic acid, the  
30 various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

- 35 Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are preferred polycarboxylate builders that can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders.

**SUBSTITUTE SHEET (RULE 26)**

Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984, Bush, issued January 28, 1986.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

#### Optional Detergent Adjuncts

As a preferred embodiment, the conventional detergent ingredients employed herein can be selected from typical detergent composition components such as detergent surfactants and detergent builders. Optionally, the detergent ingredients can include one or more other detergent adjuncts or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition. Usual detergent adjuncts of detergent compositions include the ingredients set forth in U.S. Pat. No. 3,936,537, Baskerville et al, are incorporated herein by reference. Such adjuncts which can be included in detergent compositions employed in the present invention, in their conventional art-established levels for use (generally from 0% to about 20% of the detergent ingredients, preferably from about 0.5% to about 10%), include color speckles, suds boosters, suds suppressors, antitarnish and/or anticorrosion agents, soil-suspending agents, soil release agents, dyes, fillers, optical brighteners, germicides, alkalinity sources, hydrotropes, antioxidants, perfumes, solvents, solubilizing agents, clay soil removal/anti-redeposition agents, polymeric dispersing agents, processing aids, fabric softening components static control agents, etc.

Bleach systems optionally, but preferably, will also comprise a chelant which not only enhances bleach stability by scavenging heavy metal ions which tend to decompose bleaches, but also assists in the removal of polyphenolic stains such as tea stains, and the like. Various chelants, including the aminophosphonates, available as DEQUEST from Monsanto, the nitrilotriacetates, the hydroxyethyl-ethylenediamine triacetates, and the like, are known for such use. Preferred biodegradable, non-phosphorus chelants include ethylene-diamine disuccinate ("EDDS"; see U.S. Patent 4,704,233, Hartman and Perkins), ethylenediamine-N,N'-diglutamate (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinate (HPDDS) compounds. Such chelants can be used in their alkali or alkaline earth metal salts, typically at levels from about

0.1% to about 10% of the present compositions.

Optionally, the detergent compositions employed herein can comprise, in addition to the bleaching system of the present invention, one or more other conventional bleaching agents, activators, or stabilizers which do not react with or otherwise harm natural rubber. In general, the formulator will ensure that the bleach compounds used are compatible with the detergent formulation. Conventional tests, such as tests of bleach activity on storage in the presence of the separate or fully-formulated ingredients, can be used for this purpose. A specific example of an optional bleaching agent for incorporation in this invention is tetraacetyl ethylene diamine (TAED). Such bleaching compounds and agents can be optionally included in detergent compositions in their conventional art-established levels of use, generally from 0% to about 15%, by weight of detergent composition.

Bleaching activators of the invention are especially useful in conventional laundry detergent compositions such as those typically found in granular detergents or laundry bars. U.S. Patent 3,178,370, Okenfuss, issued April 13, 1965, describes laundry detergent bars and processes for making them. Philippine Patent 13,778, Anderson, issued Sept. 23, 1980, describes synthetic detergent laundry bars. Methods for making laundry detergent bars by various extrusion methods are well known in the art.

The following examples are given to further illustrate the present invention, but are not intended to be limiting thereof.

#### EXAMPLE I

Synthesis of Nonanoyl Caprolactam - To a two litre three necked round bottomed flask equipped with a condenser, overhead stirrer and 250ml addition funnel is charged 56.6g (0.5 moles) caprolactam, 55.7g (0.55 moles) triethylamine and 1 litre of dioxane; the resulting solution is heated to reflux (120°C). A solution of 88.4g (0.5 moles) nonanoyl chloride dissolved in 200ml of dioxane is then added over 30 minutes and the mixture is refluxed for a further 6 hours. The reaction mixture is then cooled, filtered, and the solvent removed by rotary evaporation to yield 120.5g of the product as a dark oil. This crude product is then dissolved in diethyl ether, washed with 3x50ml aliquots of water, dried over magnesium sulphate and the solvent removed by rotary evaporation to yield 81.84g (65% theoretical yield) of product which is shown by NMR to be 90% pure, with the remaining material being nonanoic acid.

#### EXAMPLE II

Synthesis of Benzoyl Caprolactam - To a two litre three necked round bottomed flask equipped with a condenser, overhead stirrer and 250ml addition

funnel is charged 68.2g (0.6 moles) caprolactam, 70g (0.7 moles) triethylamine and 1 litre of dioxane; the resulting solution is heated to reflux (120°C). A solution of 84.4g (0.6 moles) benzoyl chloride dissolved in 200ml of dioxane is then added over 30 minutes and the mixture is refluxed for a further 6 hours. The reaction mixture is then cooled, filtered, and the solvent removed by rotary evaporation to yield 121.7g of the product as an oil which crystallizes on standing. This crude product is then redissolved in toluene and precipitated with hexane, yielding 103g (79% theoretical yield) of a white solid which is shown by NMR to be over 95% pure, with the remaining material being benzoic acid.

### EXAMPLE III

Synthesis of (6-nonanamidocaproyl)oxybenzenesulfonate (NACA-OBS).

6-nonanamidocaproic Acid (NACA) - The reaction is carried out in a 12L 3-necked flask equipped with a thermometer, addition funnel and mechanical stirrer. To a solution made from 212g (5.3 moles) of sodium hydroxide and 6L of water (cooled to room temperature) is added 694.3g (5.3 moles) of 6-aminocaproic acid. This mixture is cooled to 10°C and a solution of 694.3g (5.3 moles) of nonanoyl chloride in 1L of ether is added in a slow stream (about 2.5 hours) keeping the temperature at 10-15°C. During the addition, and subsequently until acidification, the reaction is maintained at pH 11-12 by periodic addition of 50% NaOH. After the addition is complete, the reaction is stirred for another 2 hours at 10°C and allowed to come to room temperature before acidification to pH 1 with conc. HCl. The precipitated product is vacuum filtered, the filter cake is washed twice with 8L portions of water and the product air dried overnight. It is then suspended in 3L of hexane, filtered and washed with an additional 3L of hexane. The product is then vacuum dried overnight (50°C, 1 mm) to give 1354 g (94%) of NACA.

Acid Chloride (NACA-Cl) - The reaction is carried out in a 5L, 3-necked flask equipped with an addition funnel, mechanical stirrer and argon sweep. To a suspension of 542g (2.0 moles) of NACA in 2L of toluene is added (in a slow stream over 30 minutes) 476g (4.0 moles) of thionyl chloride. This mixture is stirred at room temperature for four hours during which time the solids dissolve. The solution is partially evaporated (30°C, 10 mm) to remove any excess thionyl chloride leaving 905g of NACA-Cl/toluene solution (contains approximately 2 moles of NACA-Cl). An IR spectrum confirms conversion of COOH to COCl.

(6-nonanamidocaproyl)oxybenzenesulfonate (NACA-OBS) - The reactor is a 12L, 3-necked flask equipped with a condenser, mechanical stirrer and static argon supply. To the reactor are added 647g of the above NACA-Cl/toluene solution (1.43 moles), 6L of toluene and 310.8g (1.43 moles) of disodium p-phenolsulfonate

(disodium p-phenolsulfonate is previously prepared and dried in a vacuum oven before use (110°C, 0.1mm hg, 18 hours). This mixture is refluxed for 18 hours. After cooling to room temperature, the product is collected on a Buchner funnel and dried to give 725g of crude solids. The crude is taken up in 7L of refluxing 87:13 (v,v) methanol/water, filtered hot and allowed to recrystallize at room temperature. The resulting precipitate is filtered and vacuum dried (50°C, 0.1 mm) for 18 hours to give 410g (64% based on NACA) of light tan product. A trace of unreacted phenolsulfonate is indicated by the small doublets at 6.75 and 7.55 ppm in the <sup>1</sup>H spectrum. Otherwise, the spectra are consistent with expected structure and no other impurities are evident.

#### EXAMPLE IV

A granular detergent composition is prepared comprising the following ingredients.

	<u>Component</u>	<u>Weight %</u>
15	C <sub>12</sub> linear alkyl benzene sulfonate	22
	Phosphate (as sodium tripolyphosphate)	30
	Sodium carbonate	14
	Sodium silicate	3
	Lipase	0.3
20	Sodium percarbonate	5
	Ethylenediamine disuccinate chelant (EDDS)	0.4
	Sodium sulfate	5.5
	Nonanoyl caprolactam	5
	Filler* and water	Balance to 100%
25	*Can be selected from convenient materials such as CaCO <sub>3</sub> , talc, clay, silicates, and the like.	

In testing the bleaching performance and effect on natural rubber washing machine parts, the following test method is used:

Aqueous crutcher mixes of heat and alkali stable components of the detergent compositions are prepared and spray-dried and the other ingredients are admixed so that they contain the ingredients tabulated at the levels shown.

The detergent granules with bleach activator are added together with 5 lb. (2.3 kg) of previously laundered fabrics including natural rubber articles such as elastic materials, to an automatic washing machine equipped with a natural rubber sump hose. Actual weights of detergent and bleach activator are taken to provide a 950 ppm concentration of the former and 50 ppm concentration of the latter in the 17 gallon (65 l) water-fill machine. The water used has 7 grains/gallon hardness and a



pH of 7 to 7.5 prior to (about 9 to about 10.5 after) addition of the detergent and bleaching system.

The fabrics are laundered at 35°C (95°F) for a full cycle (12 min.) and rinsed at 21°C (70°F). The laundering method is repeated for 2,000 wash cycles without rupture of, or significant damage to, the natural rubber parts or without damage to the natural rubber contained in the fabrics and with good enzyme performance.

#### EXAMPLE V

A granular detergent composition is prepared comprising the following ingredients.

	<u>Component</u>	<u>Weight %</u>
10	Anionic alkyl sulfate	7
	Nonionic surfactant	5
	Zeolite (0.1-10 micron)	10
	Trisodium citrate	2
15	SKS-6 silicate builder	10
	Acrylate maleate polymer	4
	Nonanoyl caprolactam	5
	Sodium percarbonate*	15
	Sodium carbonate	5
20	Ethylenediamine disuccinate chelant (EDDS)	0.4
	Suds suppressor	2
	Protease (as SAVINASE)	0.3
	Lipase (as LIPOLASE)	0.3
	Soil release agent	0.2
25	Minors, filler** and water	Balance to 100%

\*Average particle size of 400 to 1200 microns.

\*\*Can be selected from convenient materials such as CaCO<sub>3</sub>, talc, clay, silicates, and the like.

In testing the bleaching performance and effect on natural rubber washing machine parts, the following test method is used:

Aqueous crutcher mixes of heat and alkali stable components of the detergent composition are prepared and spray-dried, and the other ingredients are admixed so that they contain the ingredients tabulated at the levels shown.

The detergent granules with bleach activator are added via the dispensing drawer together with 5 lb. (2.3 kg) of previously laundered fabrics to an automatic washing machine equipped with a natural rubber sump hose. Actual weights of detergent and bleach activator are taken to provide a 8,000 ppm concentration of the

former and 400 ppm concentration of the latter in the 17 l water-fill machine. The water used has 10 grains/gallon hardness and a pH of 7 to 7.5 prior to (about 9 to about 10.5 after) addition of the detergent and bleaching system.

5 The fabrics are laundered at 40°C (104°F) for a full cycle (40 min.) and rinsed at 21°C (70°F). The laundering method is repeated for 2,000 wash cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE VI

10 A detergent composition is prepared by a procedure identical to that of Example V, with the single exception that an equivalent amount of benzoyloxybenzene sulfonate is substituted for the nonanoyl caprolactam. The laundering method of Example V is repeated for about 1200 cycles at which time the natural rubber parts ruptures.

#### EXAMPLE VII

15 A detergent composition is prepared by a procedure identical to that of Example V, with the single exception that an equivalent amount of (6-nonanamidocaproyl)-oxybenzenesulfonate as prepared in Example III is substituted for the nonanoyl caprolactam. The laundering method of Example V is repeated for 2000 cycles without rupture of, or significant damage to, the natural  
20 rubber parts and with good enzyme stability and performance.

#### EXAMPLE VIII

A detergent composition is prepared by a procedure identical to that of Example V, with the exceptions that 15% of a 1:1:1 mixture of benzoyl caprolactam, nonanoyl caprolactam and (6-nonanamidocaproyl)oxybenzene-sulfonate as prepared  
25 following Example III is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE IX

30 A detergent composition is prepared by a procedure identical to that of Example IV, with the exceptions that 20% of a 1:1 mixture of benzoyl caprolactam and (6-nonanamidocaproyl)oxybenzenesulfonate as prepared following Example III is substituted for the nonanoyl caprolactam, the amount of sodium percarbonate is 20%, and the amount of phosphate is 0%. The laundering method of Example IV is  
35 repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE X

A detergent composition is prepared by a procedure identical to that of Example V, with the single exception that an equivalent amount of a benzoxazin-type activator is substituted for the nonanoyl caprolactam. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE XI

A detergent composition is prepared by a procedure identical to that of Example V, with the exceptions that 10% of a 1:1 mixture of a benzoxazin-type activator and tetraacetyl ethylene diamine is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 25%. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE XII

A laundry bar suitable for hand-washing soiled fabrics is prepared by standard extrusion processes and comprises the following:

	<u>Component</u>	<u>Weight %</u>
	C <sub>12</sub> linear alkyl benzene sulfonate	30
	Phosphate (as sodium tripolyphosphate)	7
	Sodium carbonate	25
20	Sodium pyrophosphate	7
	Coconut monoethanolamide	2
	Zeolite A (0.1-10 micron)	5
	Carboxymethylcellulose	0.2
	Polyacrylate (m.w. 1400)	0.2
25	(6-nonanamidocaproyl)oxybenzenesulfonate	5
	Sodium percarbonate	5
	Brightener, perfume	0.2
	Protease (as Protease C)	0.3
	Lipase (as LIPOLASE)	0.3
30	CaSO <sub>4</sub>	1
	MgSO <sub>4</sub>	1
	Water	4
	Filler*	Balance to 100%

\*Can be selected from convenient materials such as CaCO<sub>3</sub>, talc, clay, silicates, and the like.

The detergent laundry bars are processed in conventional soap or detergent bar making equipment as commonly used in the art. Testing is conducted following

the procedures and methods in Example V. The laundering method is repeated for 2,000 wash cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE XIII

5 A detergent composition is prepared by a procedure identical to that of Example XII, with the single exception that an equivalent amount of benzoyl caprolactam is substituted for the (6-nonanamidocaproyl)oxybenzenesulfonate. The laundering method of Example XII is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and  
10 performance.

#### EXAMPLE XIV

A detergent composition is prepared by a procedure identical to that of Example XII, with the single exception that an equivalent amount of nonanoyl caprolactam is substituted for the (6-nonanamidocaproyl)oxybenzenesulfonate. The  
15 laundering method of Example XII is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE XV

A granular detergent composition is prepared comprising the following  
20 ingredients.

	<u>Component</u>	<u>Weight %</u>
	Anionic alkyl sulfate	7
	Nonionic surfactant	5
	Zeolite (0.1-10 micron)	10
25	Trisodium citrate	2
	SKS-6 silicate builder	10
	Acrylate maleate polymer	4
	Nonanoyl caprolactam	5
	Sodium percarbonate*	15
30	Sodium carbonate	5
	Ethylenediamine disuccinate chelant (EDDS)	0.4
	Suds suppressor	2
	Protease (as Protease C)	0.5
	Soil release agent	0.2
35	Minors, filler** and water	Balance to 100%

Average particle size of 400 to 1200 microns.

\*\*Can be selected from convenient materials such as  $\text{CaCO}_3$ , talc, clay, silicates, and

the like.

Aqueous crutcher mixes of heat and alkali stable components of the detergent composition are prepared and spray-dried, and the other ingredients are admixed so that they contain the ingredients tabulated at the levels shown.

- 5        Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE XVI

- 10       A detergent composition is prepared by a procedure identical to that of Example XV, with the single exception that an equivalent amount of benzoyl caprolactam is substituted for the nonanoyl caprolactam.

- Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of,  
15       or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE XVII

- A detergent composition is prepared by a procedure identical to that of Example XV, with the exceptions that 15%, by weight, of (6-nonanamido-  
20       caproyl)oxybenzenesulfonate is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%.

- Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and  
25       performance.

#### EXAMPLE XVIII

- A detergent composition is prepared by a procedure identical to that of Example XV, with the exceptions that 15%, by weight, of a 1:1 mixture of (6-nonanamidocaproyl)oxybenzenesulfonate and (6-decanamidocaproyl)oxybenzene-  
30       sulfonate activator is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%.

- Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and  
35       performance.

#### EXAMPLE XIX

- A detergent composition is prepared by a procedure identical to that f

Example XV, with the exceptions that 15%, by weight, of a 1:1 mixture of (6-octanamidocaproyl)oxybenzenesulfonate and (6-decanamidocaproyl)oxybenzenesulfonate activator is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%.

- 5        Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE XX

- 10        A detergent composition is prepared by a procedure identical to that of Example XV, with the exceptions that 15%, by weight, of (6-octanamidocaproyl)-oxybenzenesulfonate is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%.

- 15        Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### EXAMPLE XXI

- 20        A detergent composition is prepared by a procedure identical to that of Example XV, with the exceptions that 15%, by weight, of (6-decanamidocaproyl)-oxybenzenesulfonate activator is substituted for the nonanoyl caprolactam and the amount of sodium percarbonate is 30%.

- 25        Testing is conducted following the procedures and methods in Example V. The laundering method of Example V is repeated for 2,000 cycles without rupture of, or significant damage to, the natural rubber parts and with good enzyme stability and performance.

#### Method of Processing the Bleach Activators

- 30        The bleach activators may be processed with a range of organic and inorganic substances to achieve a rapid dispersion in the bleaching liquor and to insure good stability in the detergent composition. The bleach activators are preferably employed in particulate form.

- 35        An example of preferred caprolactam bleach activator particles is an agglomerate of about 65%, by weight, benzoyl caprolactam; about 7% of a builder, such as aluminium silicate; about 15% sodium carbonate; about 9% dispersant, such as a polyacrylate polymer; and about 4% of a solubilizing agent, such as a linear alkyl sulfonate. Another example of a preferred caprolactam bleach activator particle is an agglomerate of about 80% to about 85%, by weight, benzoyl caprolactam and about

15% to about 20% of a binder, such as tallow alcohol ethoxylate, preferably TAE25.

An example of a preferred amido-derived bleach activator particle comprises a 1:1:1 mixture of (6-octanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)-oxybenzenesulfonate, and citric acid powder. The mixture is intimately mixed in a food mixer for 5-10 minutes. To the resultant mixture is added tallow alcohol ethoxylate (TAE25) nonionic surfactant at 50° C until granules are formed. Typically successful granulations are achieved with a ratio of bleach activator/citric acid solid mixtures:nonionic binding agent of 3.5:1. The resultant granules, ellipsoidal and spherical in shape, are white and free flowing.

A typical particle composition is about 40% to about 60%, preferably about 55%, by weight, of the bleach activator or mixture of bleach activators; about 20% to about 40%, preferably about 25%, by weight, of citric acid; and about 15% to about 30%, preferably about 20%, by weight, TAE25 binding agent. Alternatively, a 2:1 mixture of (6-decanamidocaproyl)oxybenzenesulfonate and citric acid powder may be used. In this case, the composition on the granule is 55% bleach activator, 25% citric acid, and 20% TAE25 binding agent. Other preferred organic binding agents include anionic surfactants (C<sub>12</sub> linear alkyl benzene sulfonates), polyethylene glycols, and TAE50.

Another example of a preferred amido-derived bleach activator particle comprises a 1:1:1 mixture of (6-octanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and sodium hydrogen sulfate. To the mixture is added 20% by weight of an anionic surfactant (alkyl sulfate is particularly preferred). The components are mixed into a paste with water, typically 30-50% by weight of water being added, and introduced into an air flow such that droplets are formed. This technique is commonly known as spray drying. This may be achieved using, for example a Nyro atomiser, or a spray gun. Hot air (typically 150-300 degree Celisius) is blasted upwards through a column. The resulting particles formed are collected at the bottom of the column and classified into desired size.

A typical particle composition is about 40-60%, preferably about 55%, by weight of the bleach activator or mixture of activators, about 20-40%, preferably about 25%, of sodium hydrogen sulfate, and about 15-25%, preferably about 20%, of anionic surfactant. Alternatively, a 2:1 mixture of (6-decanamidocaproyl)oxybenzenesulfonate and sodium hydrogen sulfate may be used. Citric acid or boric acid may also be used in place of sodium hydrogen sulfate in the above examples.

The particle size of the resulting granules may be varied according to the desired performance/stability. Fine particles (<250 um) show improved solubility; though coarse particles (>1180 um) are more stable in high temperatures/moist environments. A typical, preferred particle size range is 250-1180 um; particles  
5 conforming to this specification show excellent stability and solubility.

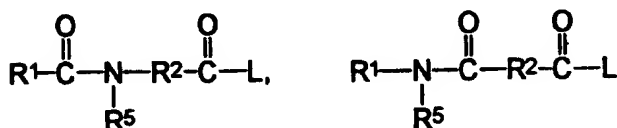
**SUBSTITUTE SHEET (RULE 26)**



## WHAT IS CLAIMED IS:

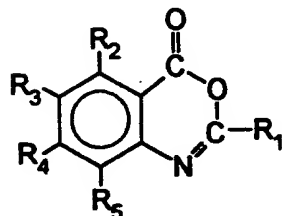
1. A detergent composition comprising an effective amount of one or more types of enzymes and a bleaching system comprising at least 0.1% by weight of a peroxygen bleaching compound capable of yielding hydrogen peroxide in an aqueous liquor and at least 0.1% by weight of one or more bleach activators, wherein said bleach activators are members selected from the group consisting of:

a) a bleach activator of the general formula:



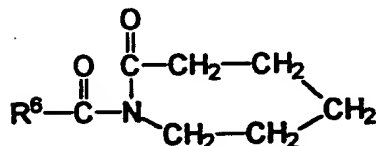
or mixtures thereof, wherein  $\text{R}^1$  is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms,  $\text{R}^2$  is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms,  $\text{R}^5$  is H or an alkyl, aryl, or alkaryl group containing from 1 to 10 carbon atoms, and L is a leaving group;

b) a benzoxazin-type bleach activator of the formula:



wherein  $\text{R}_1$  is H, alkyl, alkaryl, aryl, arylalkyl, and wherein  $\text{R}_2$ ,  $\text{R}_3$ ,  $\text{R}_4$ , and  $\text{R}_5$  may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxy, amino, alkylamino,  $-\text{COOR}_6$ , wherein  $\text{R}_6$  is H or an alkyl group and carbonyl functions;

c) a N-acyl caprolactam bleach activator of the formula:



wherein  $\text{R}^6$  is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbons; and

d) mixtures of a), b) and c).

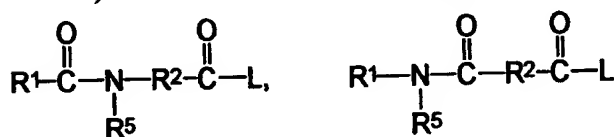
2. A composition according to Claim 1 wherein said enzymes comprise at least 0.001%, by weight of said detergent composition, and are selected from the group

consisting of proteases, amylases, lipases, cellulases, peroxidases and mixtures thereof.

3. A composition according to Claim 2 wherein said enzyme is lipase derived from the fungus Humicola lanuginosa or a modified bacterial serine protease derived from Bacillus subtilis, Bacillus lentus, or Bacillus licheniformis.

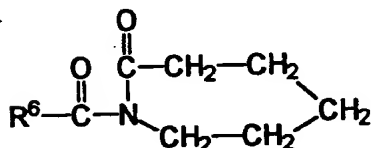
4. A composition according to Claim 2 wherein said bleach activator is selected from the group consisting of:

a) a bleach activator of the formula:



or mixtures thereof, wherein R<sup>1</sup> is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R<sup>2</sup> is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms, R<sup>5</sup> is H or an alkyl, aryl, or alkaryl group containing from 1 to 10 carbon atoms, and L is a leaving group;

b) a N-acyl caprolactam bleach activator of the formula:



wherein R<sup>6</sup> is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbons; and

c) mixtures of a) and b);

and said enzyme is selected from the group consisting of SAVINASE, Protease C, and mixtures thereof.

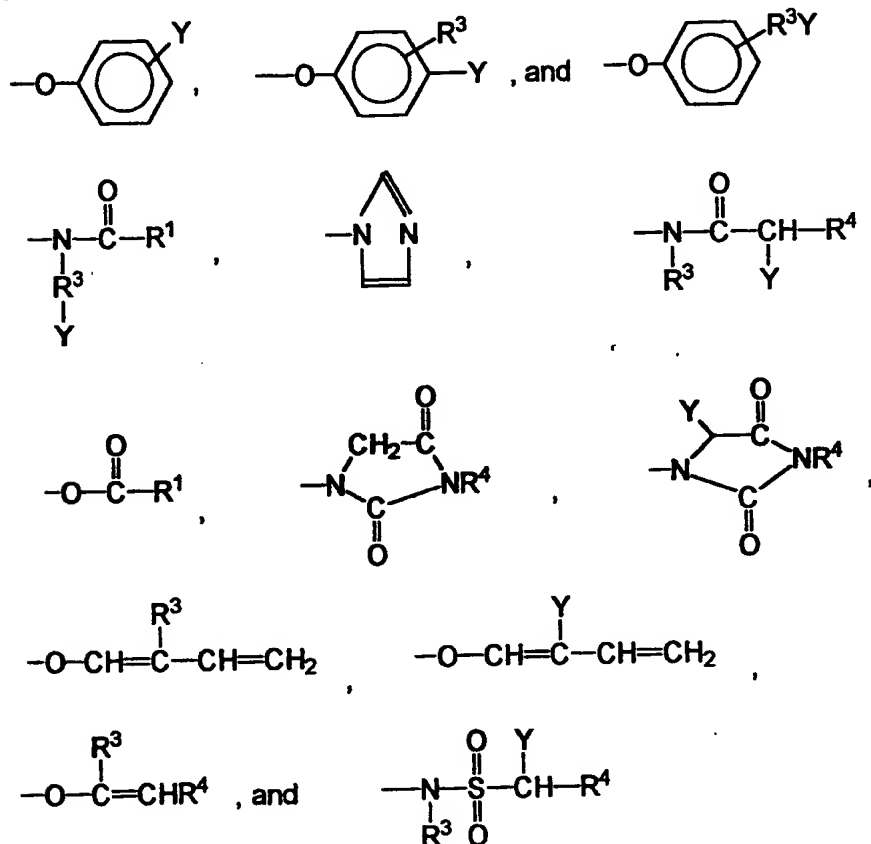
5. A composition according to Claim 1 or Claim 4 wherein said bleach activator is selected from the group consisting of benzoyl caprolactam, nonanoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, (6-octanamidocaproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzenesulfonate, and mixtures thereof; said enzyme is Protease C; and said peroxygen bleaching compound is selected from the group consisting of sodium perborate monohydrate, sodium perborate tetrahydrate, sodium

pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium percarbonate, sodium peroxide and mixtures thereof.

6. A composition according to Claim 1 or Claim 4 wherein the bleach activators are in particulate form, preferably spray dried particles.

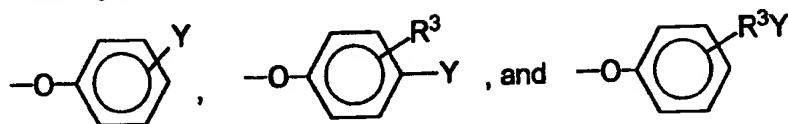
7. A composition according to Claim 1 or Claim 4 wherein the molar ratio of hydrogen peroxide to bleach activator is greater than approximately 1.0.

8. A composition according to Claim 1 wherein  $R^1$  is an alkyl group containing from 6 to 12, preferably from 7 to 10, carbon atoms;  $R^2$  contains from 1 to 8, preferably from 4 to 5, carbon atoms;  $R^5$  is H or methyl; and L is selected from the group consisting of:



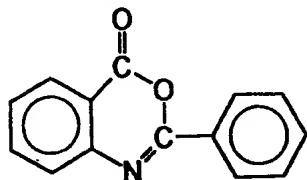
and mixtures thereof, wherein  $R^1$  is as defined in Claim 1,  $R^3$  is an alkyl chain containing from 1 to 8 carbon atoms,  $R^4$  is H or  $R^3$ , and Y is H or a solubilizing group.

9. A composition according to Claim 8 wherein L is selected from the group consisting of:



wherein  $R^3$  is an alkyl chain containing from 1 to 8 carbon atoms, Y is  $-SO_3^-M^+$  or  $-CO_2^-M^+$  wherein M is sodium or potassium.

10. A composition according to Claim 1 wherein said benzoxazin-type bleach activator has the formula:

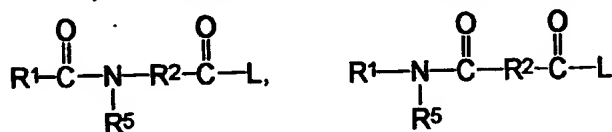


11. A composition according to Claim 1 further comprising from 5% to 80%, by weight, of a deterative surfactant; from 5% to 80%, by weight, of a deterative builder; and from 0% to 20%, by weight, of conventional deterative adjuncts.

12. A method for cleaning fabrics in an automatic washing machine having parts made of natural rubber which is susceptible to oxidative degradation, said method comprising agitating said fabrics in said machine in an aqueous liquor comprising a detergent composition according to Claim 1, such that said natural rubber parts of said machine are substantially undamaged by the detergent composition.

13. A method according to Claim 12 wherein said bleaching system comprises at least 0.1%, by weight, of one or more bleach activators, wherein said bleach activators are selected from the group consisting of:

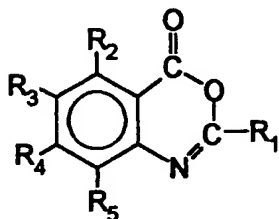
a) a bleach activator of the general formula:



or mixtures thereof, wherein  $R^1$  is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms,  $R^2$  is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms,  $R^5$  is H or an alkyl, aryl, or alkaryl group containing from 1 to 10

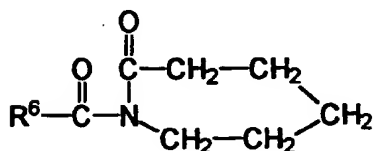
carbon atoms, and L is a leaving group;

b) a benzoxazin-type bleach activator of the formula:



wherein  $R_1$  is H, alkyl, alkaryl, aryl, arylalkyl, and wherein  $R_2$ ,  $R_3$ ,  $R_4$ , and  $R_5$  may be the same or different substituents selected from H, halogen, alkyl, alkenyl, aryl, hydroxyl, alkoxy, amino, alkylamino,  $-COOR_6$ , wherein  $R_6$  is H or an alkyl group and carbonyl functions;

c) a N-acyl caprolactam bleach activator of the formula:



wherein  $R^6$  is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbons; and

d) mixtures of a), b), and c).

13. A method according to Claim 12 wherein said bleaching system further comprises at least 0.1%, by weight, of a peroxygen bleaching compound capable of yielding hydrogen peroxide in an aqueous liquor; wherein said peroxygen bleaching compound is selected from the group consisting of sodium perborate, monohydrate, sodium perborate tetrahydrate, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium percarbonate, sodium peroxide and mixtures thereof.

14. A method according to Claim 13 wherein said enzymes comprise at least 0.001%, by weight of detergent composition, of said detergent composition and are selected from the group consisting of proteases, amylases, lipases, cellulases, peroxidases and mixtures thereof.

15. A method according to Claim 14 wherein said enzyme is lipase derived from the fungus Humicola lanuginosa or wherein said enzyme is a modified bacterial serine protease derived from Bacillus subtilis, Bacillus lentus, or Bacillus licheniformis.



wherein R<sup>1</sup> is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R<sup>2</sup> is an alkylene, arylene or alkarylene group containing from 1 to 14 carbon atoms, R<sup>5</sup> is H or an alkyl, aryl, or alkaryl group containing from 1 to 10 carbon atoms.

19. A composition according to Claim 18 wherein said enzyme is lipase derived from the fungus Humicola lanuginosa or wherein said enzyme is a modified bacterial serine protease derived from Bacillus subtilis, Bacillus lentus, or Bacillus licheniformis.

20. A composition according to Claim 18 further comprising from 5% to 80%, by weight, of a deterative surfactant, from 5% to 80%, by weight, of a deterative builder and from 0% to 20%, by weight, of conventional deterative adjuncts.

21. A method for providing enhanced dingy cleanup, said method comprising agitating said fabrics in said machine in an aqueous liquor comprising conventional detergent ingredients according to Claim 18.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 94/05372

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C11D3/39 C11D3/386

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 5 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 170 386 (PROCTER & GAMBLE) 5 February 1986 cited in the application see claims 1,2,4-15	1,2,4, 7-9,11, 18-21
X	DE,A,39 38 526 (BASF AG) 23 May 1991 see page 3, line 31 - line 54	1,10, 18-21
A	EP,A,0 403 152 (KAO CORP.) 19 December 1990 see claims; example 3	1,2,4, 18-21
P,X	WO,A,94 10284 (PROCTER & GAMBLE) 11 May 1994 see page 4, line 6 - line 15; claims; examples 3,4	1-9,11, 18-21 10
A		

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

20 September 1994

Date of mailing of the international search report

03.10.94

Name and mailing address of the ISA

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Authorized officer

Grittern, A



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 94/05372

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>EP,A,0 290 292 (PROCTER &amp; GAMBLE) 9 November 1988 see page 4, line 15 - page 7, line 20; claims 1-11 -----</p>	1,8,9,18

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US 94/05372

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0170386	05-02-86	AU-B- 584621	01-06-89
		AU-A- 4388685	02-01-86
		AU-B- 585762	22-06-89
		AU-A- 4388785	02-01-86
		CA-A, C 1254581	23-05-89
		DE-A- 3586957	18-02-93
		DE-D- 3587678	20-01-94
		DE-T- 3587678	30-06-94
		EP-A, B 0166571	02-01-86
		EP-A- 0484324	06-05-92
		JP-A- 61081498	25-04-86
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